The distillate collected in the receiver consists mainly of iodide of methyl mixed with some unaltered creosote, from which it is readily liberated by distillation, and agitation with a solution of caustic alkali.

The residue contained in the retort, on being mixed with water, now readily dissolves, with the exception of a small quantity of a heavy brown oil which contains unaltered creosote. The aqueous solution is mixed with a large quantity of water and partly saturated with carbonate of barium, the clear liquid filtered off and precipitated with acetate of lead, the white precipitate well washed and decomposed with sulphuretted hydrogen. The sulphide of lead having been filtered off, the aqueous solution is now carefully evaporated at a low temperature, when a thick heavy liquid is obtained, which in its reactions so closely resembles pyrocatechine or oxyphenic acid, that one would be inclined to consider it identical with this substance if it were not for the apparent impossibility of obtaining it in a crystalline form.

I am still engaged with the determination of the composition of the latter substance; but, from its chemical nature, so far as I have made myself acquainted with it, and from other considerations, I think it more than probable that this substance bears the closest analogy to oxyphenic acid $(C_6 H_6 O_2)$, and is in all probability its homologue.

The described decomposition of creosote may be expressed in the following way :—

$$C_8 H_{10} O_2 + HI = CH_3 I + C_7 H_8 O_2.$$

Creosote.   Iodide of methyl.
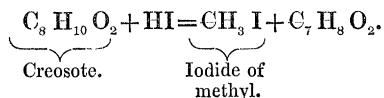
According to which creosote may be considered as methylated oxytolylic acid, or oxykressylic acid.

This view gains in probability if we consider the general properties of creosote, and the fact that a lower homologue of creosote, together with free oxyphenic acid, exists amongst the products of distillation of wood. Hlasiwetz has moreover shown that guaiacol is identical with this lower homologue of creosote, which it resembles in every respect.

If the constitution of creosote $(C_8 H_{10} O_2)$ turns out to be as stated above, guaiacol $(C_7 H_8 O_2)$ may be regarded as methylated oxyphenic acid, and we may therefore expect to obtain by the action of hydriodic acid upon this substance, iodide of methyl and oxyphenic acid.

I am about to carry out the latter experiment.

V. "Researches on the Colouring Matters derived from Coal-tar.— No. IV. Phenyltolylamine." By A. W. HOFMANN, LL.D., F.R.S. Received October 19, 1864.
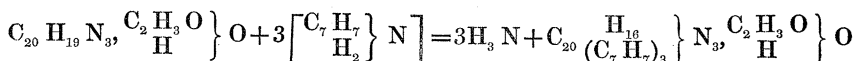
The discovery of diphenylamine among the products of decomposition furnished by the destructive distillation of aniline-blue (triphenylic ros-

aniline) which I have lately communicated to the Royal Society (Proceedings, June 16, 1864), naturally suggested the investigation of analogously constituted bodies in a similar direction. My attention has in the first place been directed to the study of a compound which, from its mode of formation, ought to be designated as toluidine-blue.

When a salt of rosaniline (the acetate for instance) is heated with double its weight of toluidine, phenomena present themselves which are similar to those observed in the analogous experiment with aniline. In the course of a few hours the rosaniline passes through all the different shades of violet, and is ultimately converted into a dark lustrous mass, which dissolves in alcohol with a deep indigo-blue colour. This substance is the acetate of tritolylrosaniline. By treatment with alcoholic ammonia, and subsequently addition of water to the solution, the free base is easily obtained, from which the several salts may be prepared by the usual processes. I have examined only one of these salts, viz. the hydrochlorate. Repeatedly crystallized from boiling alcohol, this salt is obtained in small blue crystals insoluble in water, which at 100° C. contain

$$ C_{41} H_{38} N_3 Cl = C_{20} \left. {}_{(C_7 H_7)_3}^{H_{16}} \right\} N_3, HCl. $$
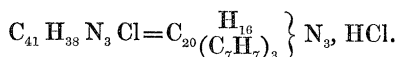
The formation of toluidine-blue is thus seen to be perfectly analogous to that of aniline-blue.

$$ C_{20} H_{19} N_3, \left. {}_{H}^{C_2 H_3 O} \right\} O + 3 \left[\left. {}_{H_2}^{C_7 H_7} \right\} N \right] = 3H_3 N + C_{20} \left. {}_{(C_7 H_7)_3}^{H_{16}} \right\} N_3, \left. {}_{H}^{C_2 H_3 O} \right\} O $$

I have not examined in detail the properties of this new series of colouring matters. Generally speaking they are more soluble than the corresponding phenyl-compounds, and therefore less easily obtained in a state of purity.

When one of these salts (the acetate for instance) is submitted to dry distillation, water and acetic acid are evolved in the first place; then follow oily products, which, as the temperature rises, become more and more viscid and ultimately solidify into crystalline masses, ammonia being abundantly evolved during the latter stages of the process. Unless the operation has been carried out on rather a large scale, a comparatively small amount of a light porous charcoal remains in the retort. The oily distillate contains several bases. Those boiling at a low temperature are almost exclusively aniline and a little toluidine. The principal portion of the products boiling at a higher temperature is a beautifully crystallized base which is easily purified. By pouring cold spirit upon the interwoven crystals, a brown mother liquor containing other bases is readily separated; the residuary substance has only to be crystallized from boiling alcohol in order to procure a compound of perfect purity.

The chemical deportment of the new substance is very similar to that of diphenylamine. Like the latter it unites with acids, forming salts of very

little stability, splitting up into their constituents under the influence of water, of heat, and even by mere exposure *in vacuo*. In contact with nitric acid the crystals at once assume a blue coloration, with an admixture of green, but nevertheless so similar to the analogous colour-reaction of diphenylamine, that by this test alone the two substances could not possibly be distinguished. The two bases differ, however, essentially in their solubility, their fusing- and boiling-points, and lastly in their composition. The new base is far less soluble in alcohol than diphenylamine; it fuses only at 87° C., while the fusing-point of diphenylamine is 45° C.; the boiling-point of the new base is 334·5° C. (corr.), at which temperature it distils without any decomposition, while diphenylamine boils at 310° (corr.).

The results of analysis lead to the formula

$$C_{13} H_{13} N.$$
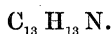
A hydrochlorate, crystallizing in little plates, and obtained by the addition of concentrated hydrochloric acid to an alcoholic solution of the base, when dried over lime, was found to contain

$$C_{13} H_{13} N, HCl.$$
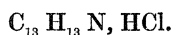
Formation and chemical deportment characterize the new base as the mixed secondary monamine of the phenyl- and tolyl-series, as phenyltolyl-amine*,

$$C_{13} H_{13} N = \left. \begin{array}{c} C_6 H_5 \\ C_7 H_7 \\ H \end{array} \right\} N.$$
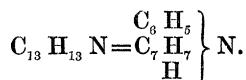
In consequence of the simultaneous existence in the molecule of the new base of the radicals phenyl and tolyl, its deportment under the influence of dehydrogenating agents became of considerable interest; and indeed, having recognized the nature of the compound, my first experiment consisted in submitting it to the action of corrosive sublimate. Both substances unite to form a dark brown mass which, after having been heated, dissolves in alcohol with a magnificent violet-blue colour. The compound thus produced exhibits the behaviour of the colouring matters generated from rosaniline by substitution. Owing to the peculiar properties of this class of substances, it would be difficult to prepare the new compound in sufficient

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* It deserves to be noticed that the percentages of carbon in diphenylamine, phenyltolylamine, and ditolylamine nearly coincide.

	Diphenylamine.	Phenyltolylamine.	Ditolylamine.
Carbon	85·21	85·24	85·28
Hydrogen	6·51	7·10	7·61

The percentages of hydrogen, however, unequivocally distinguish the three compounds. The analysis of phenyltolylamine furnished the following numbers:

	I.	II.
Carbon.........	85·10	85·11
Hydrogen ...	7·30	7·33

quantity for a detailed examination; but, judging from its mode of genera-tion, it will probably be found to be tolyldiphenylrosaniline,

$$\left.\begin{array}{c} C_{20}\,H_{16} \\ (C_6\,H_5)_2 \\ C_7\,H_7 \end{array}\right\} N_3, H_2\,O.$$
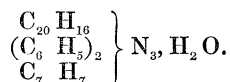
A few additional experiments performed with phenyltolylamine may still briefly be mentioned.
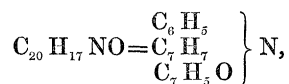
Chloride of benzoyl attacks this substance, especially on application of heat. The product of the reaction remains liquid for a long time, but, when appropriately treated with water, alkali, and spirit, it ultimately solidifies, and separates from boiling alcohol in well-formed crystals,

$$C_{20}\,H_{17}\,NO = \left.\begin{array}{c} C_6\,H_5 \\ C_7\,H_7 \\ C_7\,H_5\,O \end{array}\right\} N,$$

which are more soluble than the corresponding diphenyl-compound.

The benzoyl derivative is very readily converted into nitro substitutes. In contact with ordinary concentrated nitric acid the crystals are at once liquified, and ultimately entirely dissolve. Addition of water to this solu-tion precipitates a yellow crystalline dinitro-compound,

$$C_{20}\,H_{15}\,N_3\,O_5 = \left.\begin{array}{c} C_6\,H_4\,(NO_2) \\ C_7\,H_6\,(NO_2) \\ C_7\,H_5\;\;O \end{array}\right\} N,$$
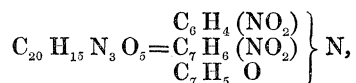
which is deposited from boiling alcohol in reddish-yellow needles. Per-fectly similar treatment converts the diphenyl body into a mononitro substi-tute. Cold fuming nitric acid, which when acting upon the diphenyl body gives rise to the formation of a dinitro-substitute, transforms the benzoy-lated phenyltolylamine into a nitro-derivative containing, according to an approximate analysis, not less than 5 atoms of NO_2.

Dinitro-phenyltolylbenzoylamide dissolves in alcoholic soda with a feebly crimson colour. Ebullition of the solution eliminates the benzoyl atom in the form of benzoate, and on cooling small yellowish red crystals,

$$C_{13}\,H_{11}\,N_3\,O_4 = \left.\begin{array}{c} C_6\,H_4\,(NO_2) \\ C_7\,H_6\,(NO_2) \\ H \end{array}\right\} N,$$
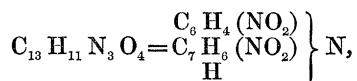
are deposited, which are easily purified by crystallization from alcohol.

Lastly, when treated with reducing agents, the dinitronated phenyl-tolyl-benzoyl compound is converted into fine white needles of a new base, to which I hope to return as soon as I shall have procured a somewhat larger supply of phenyltolylamine.
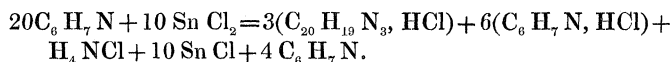
It scarcely requires to be mentioned that it is not necessary to prepare the pure toluidine-blue for the purpose of obtaining phenyltolylamine. It suffices to maintain for some hours a solution of ordinary but dried acetate of rosaniline, in its double weight of toluidine, in a flask provided with an upright condensing tube, at a boiling temperature, and to submit the violet-

blue mass produced to destructive distillation over a naked burner. The distillate is treated with hydrochloric acid, and subsequently with water, when aniline and toluidine, together with several other basic substances accompanying the phenyltolylamine, remain as hydrochlorates in solution. The oily layer which separates generally solidifies, or may be purified by rectification. The resulting crystals are crystallized from alcohol.
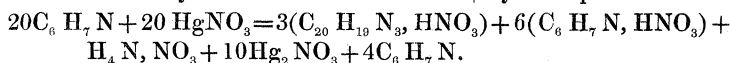
The same method is also adapted for the preparation of diphenylamine, aniline being substituted for toluidine.

If I have bestowed upon diphenylamine and phenyltolylamine rather more attention than these substances at the first glance appear to claim, I have done so in the hope of gaining additional data for the investigation of the remarkable colouring matters from which these bases are derived. Both constitution and mode of formation of these colouring matters are still involved in darkness. Theory, as it often happens, has not kept pace with practice. The anticipation I expressed in a former note, that the study of the behaviour of the colouring matters under the influence of chemical agents might disclose their true nature, has only very partially been realized. Up to the present moment, chemists have not succeeded in giving a satisfactory account either of the atomic construction of these compounds, or of the mechanism of their formation; and it would therefore scarcely be worth while to return to this question before its definite solution, unless the publication of erroneous statements by M. Schiff had threatened to divert the researches of chemists from this subject.

According to M. Schiff *, the transformation of aniline into aniline-red by means of stannic chloride is represented by the equation

$$20 C_6 H_7 N + 10 Sn Cl_2 = 3(C_{20} H_{19} N_3, HCl) + 6(C_6 H_7 N, HCl) +$$
$$H_4 NCl + 10 Sn Cl + 4 C_6 H_7 N.$$

The formation by means of mercuric nitrate† by the equation

$$20 C_6 H_7 N + 20 HgNO_3 = 3(C_{20} H_{19} N_3, HNO_3) + 6(C_6 H_7 N, HNO_3) +$$
$$H_4 N, NO_3 + 10 Hg_2 NO_3 + 4 C_6 H_7 N.$$

The latter process is accomplished at as low a temperature as 80° C., and, according to M. Schiff, is so elegant that he was enabled to make quantitative experiments. "Within a few hundredths," he says, "we have obtained the requisite quantities of the sought-for materials."

M. Schiff's equations are not conspicuous for elegance and simplicity, but they are absolutely inadmissible for other reasons. These equations utterly ignore the very essence of the process. I have pointed out, some time ago, that the formation of rosaniline involves the presence of *both aniline and toluidine.* Pure aniline furnishes no rosaniline, nor can this body be procured from pure toluidine. This fact I have since further established by many varied experiments, both on the small and on the large scale. The formation of rosaniline thus becomes the means of ascertaining rapidly the presence of toluidine. The amount of the latter

* Compt. Rend. vol. lvi. p. 271.					† Ibid. p. 545.

in crude aniline* may become so minute that its presence can no longer
be traced by distillation, or by conversion into oxalates. It may be
recognized, however, with the utmost facility by submitting the mixture to
the action of either corrosive sublimate or arsenic acid; on application of
a gentle heat the crimson colour is immediately produced.

In the equations proposed by M. Schiff there figures, moreover, ammonia
as an essential term. The existence of ammoniacal salts in the crude
rosaniline was pointed out some time ago by Prof. Bolley. But this am-
monia (which, as I have satisfied myself, is scarcely ever absent) is, accord-
ing to my opinion, not an essential product of the reaction that gives rise
to the formation of aniline-red. I have established by special and careful
experiments that appropriate treatment of a mixture of aniline and tolui-
dine with chloride of mercury at a moderate temperature is capable of
producing very considerable quantities of rosaniline without elimination of
more than a trace of ammonia. The ammonia generally observed belongs
to a different phase of the reaction, being more especially due to the
almost invariable production of a small quantity of aniline-blue.

If we wished, even now, to represent in formulæ the relation between
rosaniline and the substances which give rise to its formation, the equation

$$C_6\,H_7\,N + 2C_7\,H_9\,N = C_{20}\,H_{19}\,N_3 + 6H$$
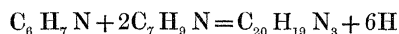
might be looked upon as an expression closely approaching truth. The
hydrogen figuring in this equation is eliminated in the form of water,
hydrochloric, hydrobromic, hydriodic acids, &c.

But even this equation gives no account of the mechanism of this re-
markable process; indeed we cannot hope for the solution of this chemical
problem before we shall have succeeded in splitting up the molecule of
rosaniline into the atomic groups which enter into its composition. It is
true its transformation into aniline- or toluidine-blue, as well as into the
several violets which are generated by the substitution of alcohol radicals,
prove even now that the rosaniline-molecule still contains three atoms of
typical hydrogen, and hence that the complex atom $C_{20}\,H_{16}$ functions in
this triamine with the value of six atoms of hydrogen; but this indeed
is the limit of the experimental evidence as yet obtained.

With regard to the number and nature of the simpler radicals into which
the carbon and hydrogen atoms of the complex atom $C_{20}\,H_{16}$ are grouped,
we can only speculate. Derived from the radicals *phenyl*, $C_6\,H_5$, and *tolyl*,
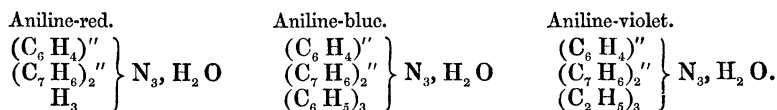$C_7\,H_7$, under the influence of dehydrogenating agents, this complex atom

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* Aniline obtained by distillation with potash from certain varieties of indigo,
is apt when treated with corrosive sublimate, to furnish traces of rosaniline. I
infer from this result that aniline thus produced contains a small proportion of
toluidine. The formation of this substance from indigo would be as readily
intelligible as the conversion under certain conditions of indigo into salicylic acid,
a fact established by Cahours's observations.

Aniline prepared from crystallized isatin does not yield a trace of rosaniline.

may possibly contain the bivalent radicals *phenylene*, $C_6 H_4$, and *tolylene*, $C_7 H_6$,

$$(C_{20} H_{16})'' = \begin{matrix} (C_6 H_4)'' \\ (C_7 H_6)'' \\ (C_7 H_6)'' \end{matrix},$$
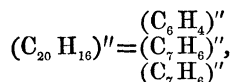
when the molecular construction of the three colouring matters might be represented by the formulæ

Aniline-red.

$$\left. \begin{matrix} (C_6 H_4)'' \\ (C_7 H_6)_2'' \\ H_3 \end{matrix} \right\} N_3, H_2 O$$

Aniline-blue.

$$\left. \begin{matrix} (C_6 H_4)'' \\ (C_7 H_6)_2'' \\ (C_6 H_5)_3 \end{matrix} \right\} N_3, H_2 O$$

Aniline-violet.

$$\left. \begin{matrix} (C_6 H_4)'' \\ (C_7 H_6)_2'' \\ (C_2 H_5)_3 \end{matrix} \right\} N_3, H_2 O.$$

We must not, however, forget that this is simply an hypothesis, and that the elements in the complex atom $C_{20} H_{16}$ may be associated in a great variety of other groups. An interesting observation quite recently made by Dr. Hugo Müller, and communicated to me by my friend while these pages are passing through the press, may possibly assist in further elucidating the nature of this class of bodies. Dr. Müller has found that rosaniline and its coloured derivatives are instantaneously decolorized by cyanide of potassium, a series of splendidly crystallized, perfectly colourless bases being produced. The composition of these bodies, which will probably be found analogous to a substance similarly obtained from harmaline by Fritzsche, remains to be established.

November 17, 1864.

Major-General SABINE, President, in the Chair.

In accordance with the Statutes, notice of the ensuing Anniversary Meeting for the election of Council and Officers was given from the Chair.

Mr. Gassiot, Dr. J. E. Gray, Dr. Hirst, Mr. Lubbock, and Dr. Odling, having been nominated by the President, were elected by ballot Auditors of the Treasurer's accounts on the part of the Society.

Among the presents announced was a Photograph of the Moon, from Mr. Warren De la Rue, respecting which an extract of a letter from the Donor was read as follows :—" Except to remove white and black spots, the photograph is untouched. The size of the original negative is about one inch, and from this was taken, in the first instance, a positive on glass nine inches in diameter. The glass positive was used for the production of four negatives, each containing a quarter of the disk. The proper distance for viewing the picture is about six feet, or two diameters."